Volume 4, issue 2, 2015 • e-ISSN: 1857-8187 • p-ISSN: 1857-8179 Research article

Occurrence of Heavy Metals in Drini Bardhë River

Agroenvironment and Ecology

Keywords: Heavy metals, Ef, Igeo, pollution, water, sediment.

Burim Haxhibeqiri		**Department of Agroenvironment and Ecology, Agricultural University of Tirana, Tirana, Albania.**
Marsela Alikaj		**Department of Biology, Faculty of Natural Sciences, "Eqrem Çabej" University, Gjirokastra – Albania.**
Ferdi Brahushi Corresponding author		**Department of Agroenvironment and Ecology, Agricultural University of Tirana, Tirana, Albania.**

Abstract

The occurrence of heavy metals in water ecosystems and sediment can impact human life, due to their possible transfer to food chain and adverse effects. Therefore, it is crucial the evaluation of the status of heavy metals in water and sediments in order to evaluate water quality and their environmental impacts. Current study aims to evaluate the occurrence of heavy metals in water and sediment as well as the water and sediment pollution of Drini Bardhë River in Kosovo. Three representatives sampling sites were selected along Drini Bardhë River to collect water and sediment samples. Heavy metals concentrations in water and sediment samples were determined by using atomic absorption spectrophotometer (AAS). The data of heavy metal concentration in water were compared with EC Directives 75/440/EEC and 2008/105/EC in order to evaluate water quality. The degree of sediment pollution was evaluated by using Enrichment Factor (EF) and Geo-accumulation Index (Igeo). Based on obtained data of heavy metals concentration in water, the values of iron and arsenic were over acceptable values of EC directives. Enrichment factor (Ef) calculations showed that sediments have moderate severe enrichment for Cd and Ni, minimal enrichment for Cu, Cr, and Pb, whereas no enrichment for Fe, Mn and Zn. Based on Geo-accumulation Index (Igeo) calculations sediments result strongly polluted with Cd and Ni, moderately polluted with Cr, unpolluted to moderately polluted with Cu, Mn, Pb and Zn, and unpolluted with Fe. The Occurrence of heavy metals in water and sediments indicates potential risk of some heavy metals as their amounts were over acceptable limits.

1. Introduction

The assessment of various substances, such are heavy metals in water and sediments, is also important for the categorization of the environmental status of the water ecosystems [15]. Through the pollution of water and sediments by heavy metals, the historical pollution of those ecosystems is defined since heavy metals cannot degrade and continuously keep on depositing in sediments [2, 6]. Monitoring of the contamination of water and sediments by heavy metals is very important, because heavy metals may accumulate to toxic levels in water ecosystems without any visible signs. Thus, high level of heavy metals in water and sediment can impact not only aquatic organisms but also all organisms and human life due to transfer through food chain [9, 17]. The human activity increases the amount of chemical substances and heavy metals in water environments [1]. Industrial waste and uncontrolled discharges of sewage has caused contamination of ecosystem with elements such as copper, chromium, manganese, lead, cadmium, zinc, nickel, etc. High concentrations of heavy metals in the water can have negative effects on yield of crop, food quality and safety of public health [13]. Most heavy metals from anthropogenic activities accumulate in sediments of rivers, where they are absorbed by clay and other materials, causing serious changes in ecosystems to organisms living in natural aquatic systems [5, 7, 14]. Therefore it is necessary participation of human activity in various natural processes in order to execute the application of various methods for the preservation and protection of many processes in nature.

This study was carried out to determine the occurence of heavy metals in water and sediments of Drini Bardhë River and to evaluate the degree of pollution by heavy metals. Such assessment would define the situation of this ecosystem, because heavy metals are serious pollutants in aquatic environments, in terms of their toxicity and ability to be incorporated in food chains [5].

2. Material and Methods

2.1. Water and sediment samples

Along Drini Bardhë River in Kosovo three representative sampling sites were selected to collect water and sediment samples (Figure 1). In each sampling site, three water and sediment samples were collected for further analysis. Standard procedure was applied for water sediment sampling. After collection, water and sediment samples were prepared and analyzed immediately to determine physical and chemical properties and heavy metals concentrations. ISO standard methods were used for determination of physical and chemical properties of water and sediments [10, 11, 12]. The concentrations of heavy metals were determined by atomic absorption spectrophotometer (AAS).

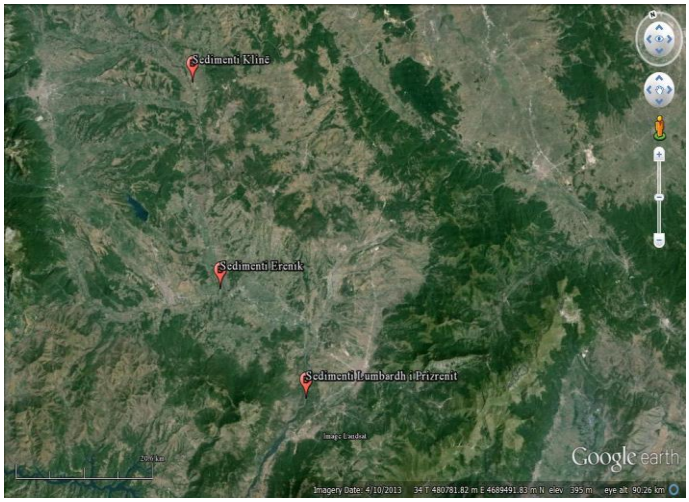

Figure 1. Water and **s**ediment sampling sites along Drini Bardhë River

2.2. Assessment of heavy metal contamination

Level of water pollution with heavy metals is evaluated based on comparison with recommended limit values for surface water by Directives 75/440/EEC and 2008/105/EC [3, 4]. Assessment of heavy metals pollution was defined using Enrichment Factor (EF) based on the following categorization: 1) Ef ≤1 no enrichment; 2) 1 < Ef ≤3 minimal enrichment; 3) 3 < Ef ≤5 moderate enrichment; 4) 5 < Ef ≤10 moderately severe enrichment; 5) 10 < Ef ≤25 severe enrichment; 6) 25 < Ef ≤50 very severe enrichment; 7) Ef > 50 extremely severe enrichment.

Follwing categorization of Geo-accumulation Index (Igeo) were used to assess sediment pollution with heavy metals: 1) Igeo < 0 unpolluted; 2) 0 ≤ Igeo < 1 unpolluted to moderately polluted; 3) 1 ≤ Igeo < 2 moderately polluted; 4) 2 ≤ Igeo < 3 moderately to strongly polluted; 5) 3 ≤ Igeo < 4 strongly polluted; 6) 4 ≤ Igeo < 5 strongly to very strongly polluted; 7) Igeo ≥ 5 very strongly polluted. The EF was calculated using the formula according [13] and Igeo by using the equation given by [8]. The heavy metals concentration in the earth crust are taken from, [16].

3. Results and Discussion

3.1. Heavy metals in water

The obtained data on heavy metals concentration in water are presented in the Table 1. These data are presented as average values of three water samples for each sampling site.

Table 1. Heavy metals concentration (mg/l) in water of Drini Bardhë River

Heavy	Water samples							Limit values of 75/440/EEC and 2008/105/EC*
metal	W1	W2	W3	Min	Max	Average	StDev	Directives
As	0.068	0.068	0.067	0.067	0.068	0.068	0.001	0.05
Cu	0.037	0.035	0.03	0.03	0.037	0.034	0.004	0.05
Cr	0.055	0.041	0.032	0.032	0.055	0.043	0.012	0.05
Fe	0.460	0.430	0.410	0.410	0.460	0.433	0.025	0.30
Mn	0.031	0.035	0.028	0.028	0.035	0.031	0.004	0.05
Ni	0.004	0.004	0.004	0.004	0.004	0.004	0.000	*0.02
Pb	0.011	0.012	0.010	0.010	0.012	0.011	0.001	0.05
Zn	0.139	0.153	0.131	0.131	0.153	0.141	0.011	3.00

Obtained data on heavy metal concentration in water samples showed that all these metals are present in this water ecosystem. The concentration of iron and zinc were higher than other metals as they are most present in natural minerals and soils. The values of arsenic and iron were higher than recommended limit values on Directives 75/440/EEC and 2008/105/EC [3, 4] for surface waters, whereas other heavy metals were under these limit values.

3.2. Sediment properties

The chemical and physical properties of sediment were estimated for a better assess of water ecosystem of Drini Bardhë River and possible relationship with heavy metal content. The data on chemical and physical properties of sediment are showed in Table 2.

Table 2. Chemical and physical properties of sediment samples.

Properties	Measurement unit	Sediment samples						
		S1	S2	S3	Min	Max	Average	StDev.
$pH_{(H2O)}$		7.4	7.9	7.4	7.4	7.9	7.6	0.3
$pH_{(KCl)}$		6.6	7.0	6.7	6.6	7.0	6.8	0.2
Humus	%	4.2	2.0	3.3	2.0	4.2	3.2	1.1
N_{total}		0.2	0.1	0.2	0.1	0.2	0.2	0.1
P_2O_5	mg/kg	165.3	130.2	761.8	130.2	761.8	352.5	355.0
K_2O		241.5	211.0	239.5	211.0	241.5	230.7	17.1
P_{total}		297.4	333.7	961.3	297.4	961.3	530.8	373.3
K_{total}		1904.0	778.3	4216.0	778.3	4216.0	2299.4	1752.7

The analysis of nutrient content indicated that these sediment samples were rich on nitrogen, phosphorus and potassium. This could be due to accumulation of nutrient and organic materials at bottom of water river. The pH values showed neutral reaction of these sediment samples.

3.3. Heavy metals in sediments

The results of heavy metal concentrations in sediment samples and calculated values of Enrichment Factor (EF) and Geo-accumulation Index (Igeo) are presented in the Table 3.

Table 3. Heavy metal concentrations in sediment samples (mg/kg)

Heavy metal	Sediment samples								
	S1	S2	S3	Min	Max	Average	StDev	Ef	Igeo
Cd	0.7	0.1	1.0	0.1	1.0	0.6	0.4	6.1	3.20
Cu	14.5	20.5	48.1	14.5	48.1	27.7	17.9	1.1	0.73
Cr	43.1	265.4	53.6	43.1	265.4	120.7	125.4	1.4	1.09
Fe	14515.5	24430.9	23116.3	14515.5	24430.9	20687.6	5385.4	0.6	-0.17
Mn	220.8	409.1	458.8	220.8	458.8	362.9	125.6	0.7	0.01
Ni	78.1	787.0	59.0	59.0	787.0	308.1	414.9	7.0	3.39
Pb	16.3	11.6	30.3	11.6	30.3	19.4	9.7	1.1	0.78
Zn	38.1	44.4	99.4	38.1	99.4	60.7	33.7	0.9	0.36

Based on the categorization of Enrichment Factor (EF) and obtained calculated values result no enrichment for Fe, Mn and Zn; minimal enrichment for Cu, Cr and Pb; moderately severe enrichment for Cd and Ni. Pollution level by heavy metals in sediments was assessed based on obtained calculated values of Igeo (HUU *et al*., 2010). According to our obtained data the sediments result unpolluted with Fe; unpolluted to moderately polluted with Cu, Mn, Pb and Zn; moderately polluted with Cr; strongly polluted with Cd and Ni. Therefore, the heavy metals Cd and Ni present a high risk for this water ecosystem. Furthermore, the rapport between heavy metals concentrations in sediment and water was calculated (Table 4) in order to asses relationship between heavy metals concentrations in sediment and water.

Table 4. Rapport between of heavy metal concentrations in sediment and water samples

Heavy	Sediment/Water samples						
metal	S1/W1	S2/W2	S3/W3	Min	Max	Average	StDev
Cu	391.89	585.71	1603.33	391.89	1603.33	860.31	650.73
Cr	783.64	6473.17	1675.00	783.64	6473.17	2977.27	3060.17
Fe	31555.43	56816.05	56381.22	31555.43	56816.05	48250.90	14460.33
Mn	7122.58	11688.57	16385.71	7122.58	16385.71	11732.29	4631.72
Ni	19525.00	196750.00	14750.00	14750.00	196750.00	77008.33	103726.81
Pb	1542.10	1002.59	2944.61	1002.59	2944.61	1829.77	1002.46
Zn	274.10	290.20	758.78	274.10	758.78	441.03	275.30

Obtained data showed that iron and nickel present the highest rapport values, showing that these heavy metals tend to be more accumulated in sediments than water samples compare to the other heavy metals. This fact is related also with origin of sediment by natural earth material and high concentration of iron and nickel in these materials.

4. Conclusions

Heavy metals were present in water and sediments of Drini Bardhë River. Their amounts vary according to sampling site and analyzed heavy metal. In water, only the amounts of arsenic and iron were higher than recommended limit values based on Directives 75/440/EEC and 2008/105/EC for surface waters.

In sediment their amounts were in this following order: Fe>Mn> Zn>Cu> Pb> Cr >Cd> Ni. Enrichment factor calculations showed that in sediment were observed moderate severe enrichment for Cd and Ni, minimal enrichment for Cu, Cr, and Pb, whereas no enrichment for Fe, Mn and Zn. Furthermore, based on Igeo calculations sediments result strongly polluted with Cd and Ni, moderately polluted with Cr, unpolluted to moderately polluted with Cu, Mn, Pb and Zn, and unpolluted with Fe.

High rate of Cr, Cd and Ni in these sediments can affect the quality of water and potential adverse effect due to their possible transfer in food chain.

References

1. Alikaj M., Brahushi F., Rada Z., 2014. Heavy metals contamination of the sediments in the Viroi lake of Gjirokastra district, Albania. Thalassia Salentina, Volume 36: 35-42. ISSN 0563-3745, e-ISSN1591-0725, DOI 10.1283/i15910725v36p35.
2. Alloway JB., 1995. Soil pollution and land contamination. In: Harrison RM (Ed). Pollution: Causes, effects and control. The Royal Society of Chemistry, Cambridge
3. Council Directive 75/440/EEC of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States as amended by Council Directive 79/869/EEC (further amended by Council Directive 81/855/EEC and Council Regulation 807/2003/EC) and both amended by Council Directive 91/692/EEC (further amended by Regulation 1882/2003/EC).
4. Directive 2008/105/EC of The European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. L 348/84 Official Journal of the European Union.
5. El Nemr A., 2003. Assessment of heavy metal pollution in surface muddy sediments of lake Burullus southeastern Mediterranean, Egypt, Egypt. J. Agual. Biol & Fish., VoL7, No.4:67-90, ISSN 1110-6131.
6. Forstner, U., 1990. Contaminated sediments. Lecture Notes in Earth Science, vol. 21, Springer-Verlag, Berlin.
7. Ghrefat H, Yusuf N. 2006. Assessing Mn, Fe, Cu, Zn and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. Chemosphere 65: 2114–2121.
8. Huu Hieu Ho, Rudy Swennen, and An Van Damme 2010. Distribution and contamination status of heavy metals in estuarine sediments near cua ong harbor, ha long bay, Vietnam. Geologica belgica, 13/1-2: 37-47.
9. Hakanson, L. 1980. An ecological risk index for aquatic pollution control. Sedimentological approach. Water Research, 14: 975-1001. doi:10.1016/0043-1354(80)90143-8.
10. ISO 10390.1994. Soil quality- Determination of pH. International organization for standartization. Geneva, Switzeland. 5p.
11. ISO 13878 (1998). Soil Quality – Determination of total nitrogen content by dry combustion ("Elemental analysis"). International Organization for Standardization. Geneva, Switzerland. 5p.
12. ISO 14235, Soil quality- Determination of organic carbon by sulfochromic oxidation.

13. Li Yu, Gou Xin, Wang Gang, Zhang Qiang, Su Qiong, and Xiao Guoju, 2008. Heavy metal contamination and source in arid agricultural soil in central Gansu Province. China Journal of Environmental Sciences, 20: 607–612
14. MacFarlane, G.R., Burchett, M.D., 2000. Cellular distribution of Cu, Pb and Zn in the Grey Mangrove Avicennia marina (Forsk.). Vierh. Aquat. Bot. 68, 45–59.
15. Miho A., Cullaj A., Hasko A., Lazo P., Kupe L., Bachofen R., Brandi H., Schanz F. and Baraj B., 2005. Environmental state of some rivers in Albanian Adriatic lowland. 34 – 37.
16. Rudnick, R.L., and Gao, S., 2005. Composition of the Continental Crust: In: Celo V. (Ed.). The Crust (pp. 1-64). Amsterdam-San Diego-Oxford-London: Elsevier.
17. Schuurmann, G., Market, B., 1998. Ectotoxicology, Ecological Fundamentals, Chemical Exposure, and Biological Effects. John Wiley & Sons Inc, and Spektrum Akademischer Verlag.